THE ESTIMATION OF SULPHUR IN RUBBER

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Sulphur may be present in vulcanised rubber in the following forms:-

1. Free Sulphur;
2. Combined Sulphur;
   (a) Sulphur in organic combination, i.e., sulphur combined with caoutchouc, in resins and proteins, in rubber substitutes, in mineral rubber, and in organic accelerators.
   (b) Sulphur in inorganic combination, i.e., as metallic sulphides, sulphates, and, occasionally, as sulphites.

Free sulphur and sulphur combined with caoutchouc are always present, and, in the majority of cases, there is some sulphide or sulphate, which may have been added as such or formed during vulcanisation. The method adopted to determine either the total sulphur or the sulphur present in any of the above-mentioned forms depends on the composition of the rubber in question, and, if the composition of the /

the mixing is not known, any quantitative determination must be preceded by a qualitative examination.

This thesis deals mainly with the estimation of total sulphur; the determination of free sulphur is at present being studied, and only an outline of the methods pursued in this latter connection and a few of the results obtained are given: it is hoped to publish the results more fully at a subsequent date.

Total Sulphur

The term "total sulphur" is generally used in rubber practice to denote the total amount of elemental sulphur added as such to effect vulcanisation, and in this sence it is a value of great importance. In this thesis the term will include all sulphur present in the mixing, whether added originally in the elemental state or as a sulphur-containing compound, with the sole exception of sulphur added as barium sulphate.

In the laboratories of many rubber factories, total sulphur is at present determined by the Carius method for the estimation of sulphur in organic compounds. This method gives results of dependable accuracy but is too tedious for routine purposes, and many /

many attempts have, therefore, been made to devise a method of greater rapidity but still comparable in accuracy with the Carius method. This thesis is, in part, the outcome of one such attempt.

Preliminary Experiments.

It was necessary, in the first instance, to prepare a series of vulcanised rubber standards containing varying proportions of sulphur and involving the commoner "fillers." The method employed in preparing these standard samples was, briefly, as follows:-

The required quantities of crude rubber, filler, and sulphur are first weighed out with moderate accuracy. The rubber is then repeatedly passed through the heated rolls of an experimental mixing mill, and the latter are gradually tightened up until the rubber is in a thoroughly plastic condition. The sulphur and drugs are then gradually worked in, the aim being to obtain as homogeneous a "dough" as possible. This is accomplished by scattering a part of the sulphur and fillers (in a finely powdered state) over the sheet of plastic rubber travelling round the front roll, cutting or tearing the sheet away, folding and refolding, again working on the rolls, scattering on more /

more of the fillers, and so on, until the non-rubber ingredients are distributed as evenly as possible throughout the batch. A portion of the dough is then placed between sheets of tin-foil in a cast-iron mould, and is cured for a suitable time at a convenient steam pressure between the plattens of a hydraulic vulcanising press.

The compositions of the samples prepared in this manner are detailed in Table 1.

Table 1 /

Table 1.

Mixing Number	Drug	Parts by Weight: Drug	Plantation Sheet	Sulphur	Time of Cure in mins. @ 50 lbs. Steam
E.1681	-	-	100	8	150
E.1682	Zinc oxide	100	100	8	150
E.1683	Whiting	100	100	8	150
E.1684	Barytes	100	100	8	150
E.1685	Lithopone	100	100	8	150
E.1686	Carbon black	100	100	8	150
E.1687	China clay	100	100	8	150
E.1688	Hydrocarbon	10	100	8	180
E.1689	Magnesia	25	100	8	120
E.1690	Red Oxide of Iron	10	100	8	120
E.1691	Ultramarine	10	100	8	150
E.1692	Antimony sulphide	10	100	8	120
E.1693	Lime	2	100	8	120
E.1694	Litharge	100	100	8	60
E.1694/1	"	20	100	8	60
E.1695	Heavy Calcined Magnesia	2	100	8	120
E.1703	Calcium sulphate	100	100	8	150
E.1704	Silica	100	100	8	150
E.1705	-	-	65	35	330
E.1706	Lime Whiting	12 30	38	20	105
E.1713	French chalk	100	100	8	150
E.1730	White Factice	20	100	8	180
E.1731	Brown Factice	20	100	8	150

The standard mixings prepared in this way were calibrated by analysis for total sulphur by the Carius method, which must now be outlined:-

A weighed portion of the finely divided sample is heated with fuming nitric acid in a sealed tube of hard glass for 3 hours at 220°C. On cooling, the pressure /

pressure is released by melting the point of the sealed tube. The end of the tube is then cut off and the contents and washings transferred to an evaporating basin. About 2 grams of pure sodium chloride are stirred in and the contents of the basin evaporated to dryness on the steam bath. 10 ccs. of concentrated hydrochloric acid are then added and the liquid is again taken to dryness. The residue is moistened with 2 or 3 ccs. of concentrated hydrochloric acid, taken up with hot distilled water, filtered, made up to about 250 ccs., and heated to boiling. The sulphate is then precipitated by running in, drop by drop, a moderate excess of a hot normal solution of barium chloride. The mixture is set aside overnight and filtered hot through a double filter paper. The barium sulphate is then washed with hot water until the washings are free from chloride, and ignited. The precipitate is then treated with a drop of concentrated sulphuric acid and a few drops of alcohol, carefully dried, and ignited to constant weight.

"Blank" analyses had to be made to allow for sulphur in the analytical reagents. Four such estimations yielded respectively .0051, .0045, .0041, .0048 gram of residue - average .0046 gram.

Ferric /

Ferric ions interfere with the gravimetric estimation of sulphate, ferric sulphate being adsorbed by the barium sulphate during precipitation; on ignition this yields ferric oxide by volatilisation of sulphur trioxide. Accordingly in the analysis of the mixing containing as pigment red oxide of iron, the ferric ions were removed from solution by precipitating as ferric hydroxide and filtering, before precipitation of barium sulphate.

After oxidation of a mixing containing litharge, the sulphur would be present to a considerable extent as lead sulphate, and, owing to the insoluble nature of this compound, would be removed in the filtration preceding precipitation with barium chloride. This difficulty is surmounted by a modified method due to Mr Neil T. Hay:-

After oxidation of the sample in the Carius tube, and successive evaporations of the liquid with sodium chloride and concentrated hydrochloric acid, the residue is taken up with water and a few drops of concentrated hydrochloric acid, heated to boiling, filtered through a tared filter paper, and washed thoroughly with hot water, the washings being added to the filtrate. In the filtrate the sulphate is estimated by precipitation with barium chloride in the usual /

usual way. The tared filter paper and contents are dried in the steam oven and weighed to constancy. The filter paper is then replaced in the funnel and washed with a boiling solution of ammonium acetate until the washings give no precipitate with potassium chromate. The loss in weight of the contents of the tared filter paper gives the amount of sulphur present as lead sulphate.

Before the analytical figures for the sulphur contents of the standard mixings could be compared with their intended compositions, some further estimations had to be performed.

In the first place, determinations were made by the Carius method of the total sulphur in the sulphur and rubber used in compounding.

The results of four such analyses on the crude rubber (Plantation Sheet) were 0.04%, 0.07%, 0.09%, 0.10% - mean 0.08%.

Estimations of the purity of four samples of sulphur gave 99.7%, 99.9%, 100.2%, 100.3% - average purity 100.0%.

Then, sulphur is present as a constituent of either the pure substance or of an impurity in certain of the "fillers" used. Accordingly, samples of each of /

of these substances were analysed for total sulphur by the Carius method, and the results obtained are detailed in Table 2.

(N.B. In the case of barytes, only the "soluble" sulphur is thereby included in the estimation, i.e., that present as impurity, e.g., calcium sulphate.)

Table 2.

Filler	Results (%)	Mean (%)
Barytes	0.25 0.25	0.25
Calcium sulphate	20.3 20.4	20.4
Lithopone	8.85 8.91	8.88
Zinc oxide	0.11 0.10	0.11
Ultramarine	10.4 10.4	10.4
Antimony sulphide	26.1 26.3	26.2
Litharge	0.07 0.07	0.07
Bitumen	2.82 2.77	2.80
White Factice	8.71 8.72	8.72
Brown Factice	18.4 18.4	18.4

No figures for whiting, carbon black, china clay, magnesium $K_2Cr_2O_7$, lime, calcined magnesia, silica or Prussian blue.

By /

By correlating the results of these latter analyses with the pre-arranged compositions of the standard samples, "theoretical" figures were derived for the total sulphur contents of these mixings.

It was then necessary to estimate the accuracy with which mixings of required composition could be prepared with the apparatus at our disposal. Previous work indicated that, of the common "fillers", barytes is the one least likely to affect sulphur estimations on the vulcanised "compound." Accordingly, 10 similar mixings, each containing 100 parts of rubber, 100 parts of barytes, and 8 parts of sulphur, were separately compounded and cured. An uncured and a cured sample of each mixing were then analysed by the Carius method. The results are given in Table 3.

8/208 = 3.85 %

Table 3 /

Table 3.

Mixing Number	Calculated %age	Uncured Stock: Analytical %ages	Uncured Stock: Mean %	Cured Stock: Analytical %ages	Cured Stock: Mean %	Difference between Cured and Uncured	Difference between Cured and Calculated	% Difference between Cured and Calculated
E.1684/1	4.00	4.02 3.98	4.00	4.03 4.06	4.05	+0.05	+0.05	+1.25
E.1684/2	4.00	4.01 4.04	4.03	4.06 4.06	4.06	+0.03	+0.06	+1.50
E.1684/3	4.00	4.04 3.99	4.02	3.99 4.05	4.02	0.0	+0.02	+0.50
E.1684/4	4.00	3.99 3.92	3.96	3.99 3.96	3.98	+0.02	-0.02	-0.50
E.1684/5	4.00	4.08 3.99	4.04	4.08 4.06	4.07	+0.03	+0.07	+1.75
E.1684/6	4.00	3.97 3.98	3.98	3.94 3.98	3.96	-0.02	-0.04	-1.00
E.1684/7	4.00	4.01 4.01	4.01	3.94 4.01	3.98	-0.03	-0.02	-0.50
E.1684/8	4.00	4.03 3.96	4.00	4.07 3.98	4.03	+0.03	+0.03	+0.75
E.1684/9	4.00	3.99 4.00	4.00	4.04 3.97	4.01	+0.01	+0.01	+0.25
E.1684/10	4.00	3.91 3.99	3.95	4.01 3.97	3.99	+0.04	-0.01	-0.25

It is of interest to note that the differences between the sulphur contents of cured and uncured stocks were negligible - apparently no appreciable quantity of sulphur is lost during curing.

The greatest deviation between calculated and analytical figures for cured stocks is 1.75% of the sulphur content. We can, therefore, ascribe an accuracy range of 2% to the milling operations.

The figures obtained in the systematic analyses to calibrate the standard mixings can now be considered - these are detailed in Table 4. The possible error of the calculated percentages was taken in each case to be 2% of the intended total sulphur content.

Table 4 /

Table 4.

Mixing Number	Calculated %age	Possible Error of calculated %age	Analytical Results (%)	Mean Analytical %age	Difference between calculated & analytical %ages
E.1681	7.48	±.15	7.34 7.37 7.35 7.36	7.36	-.12
E.1682	3.93	±.08	3.94 3.97 3.92 3.84	3.92	-.01
E.1683	3.88	±.08	3.72 3.69 3.74 3.70	3.71	-.17
E.1684	4.00	±.08	4.03 4.06 4.07 4.04	4.05	+.05
E.1685	8.15	±.16	8.29 8.27 8.29 8.32	8.29	+.14
E.1686	3.88	±.08	3.73 3.68 3.70 3.67	3.70	-.18
E.1687	3.88	±.08	3.58 3.61 3.58 3.59	3.59	-.29
E.1688	7.08	±.14	6.94 7.00 7.00 6.98	6.98	-.10
E.1689 /					

Table 4 (Contd.)

Mixing Number	Calculated %age	Possible Error of calculated %age	Analytical Results (%)	Mean Analytical %age	Difference between calculated & analytical %ages
E.1689	6.07	±.12	5.93 5.93 5.92 5.97	5.94	-.13
E.1690	6.85	±.14	6.43 6.47 6.48 6.47	6.46	-.39
E.1691	7.73	±.15	7.60 7.57 7.63 7.62	7.61	-.12
E.1692	9.07	±.18	8.72 8.64 8.68 8.69	8.68	-.39
E.1693	7.35	±.15	6.98 7.08 7.02 7.06	7.04	-.31
E.1694	3.91	±.08	4.01 3.96 3.94 4.03	3.99	+.08
E.1694/1	6.32	±.13	6.31 6.38 6.26 6.31	6.29	-.03
E.1695	7.35	±.15	7.28 7.31 7.30 7.32	7.30	-.05

E.1703 /

Table 4 (Contd.)

Mixing Number	Calculated %age	Possible Error of calculated %age	Analytical Results (%)	Mean Analytical %age	Difference between calculated & analytical %ages
E.1703	13.7	±.27	13.6 13.5 13.5 13.6	13.6	-.10
E.1704	3.88	±.08	3.72 3.72 3.66 3.66	3.69	-.19
E.1705	35.1	±.70	33.9 34.0 34.1 34.1	34.0	-1.1
E.1706	20.0	±.40	19.6 19.6 19.7 19.6	19.6	-.40
E.1713	3.88	±.08	3.67 3.70 3.64 3.66	3.67	-.21
E.1730	7.68	±.15	7.50 7.54 7.54 7.55	7.54	-.14
E.1731	9.19	±.18	8.96 9.03 8.96 9.06	9.00	-.19

In several cases the discrepancy between calculated /

calculated and analytical figures is outwith the range of accuracy ascribed to the milling operations. These cases will now be considered individually.

Despite the modification in analytical procedure, the results obtained on analysis of a mixing containing ferric oxide were still low. This can, however, be explained. Excess of ammonia must be added to render the precipitation of ferric hydroxide complete, and, as this excess is subsequently neutralised with hydrochloric acid, the solution from which the barium sulphate is precipitated contains a considerable amount of ammonium chloride; ammonium sulphate is consequently carried down on addition of barium chloride and is volatilised during ignition of the precipitate. Further, it is often a matter of difficulty to wash a precipitate of ferric hydroxide free from sulphates. This latter source of error would be removed by precipitating the barium sulphate on top of the ferric hydroxide, and then redissolving the latter in the minimum quantity of hydrochloric acid. This procedure was followed in a subsequent series of analyses, but even lower results were obtained, probably because any added hydrochloric acid in excess of that necessary to redissolve the ferric hydroxide would increase /

increase the solubility of the barium sulphate in the mother liquor.

Low results were also obtained with mixings containing carbon black, China clay, silica and French chalk. Further samples containing these "fillers" were prepared according to the mixings outlined in Table 5.

Table 5.

Mixing Number	Drug	Parts by Weight			Time of Cure in mins. @ 50 lbs. Steam
		Drug	Plantation Sheet	Sulphur	
E.1686/1	Carbon black	50	100	8	150
E.1687/1	China clay	50	100	8	150
E.1704/1	Silica	50	100	8	150
E.1713/1	French chalk	50	100	8	150

Each of these samples was analysed by the Carius method and the results are given in Table 6.

Table 6 /

Table 6.

Mixing Number	Calculated %age	Possible Error of calculated %age	Analytical Results (%)	Mean Analytical %age	Difference between calculated & analytical %ages.
E.1686/1	5.11	±0.10	4.98 5.00	4.99	-0.12
E.1687/1	5.11	±0.10	4.87 4.86	4.87	-0.24
E.1704/1	5.11	±0.10	4.99 4.94	4.97	-0.14
E.1713/1	5.11	±0.10	4.95 4.92	4.94	-0.17

In each case low results were again obtained. The suggested explanation, in this instance, is that each of these substances leaves, at the conclusion of the oxidation, a residue insoluble in acids and tending to adsorb salts such as sulphates, which would not be completely removed by washing.

Carbon Black?

Further, it is noteworthy that all mixings containing calcium compounds gave low results with the exception of E.1703 - containing calcium sulphate. In these cases, on the completion of the oxidation, the solution contains a considerable amount of calcium sulphate, and it is very feasible that this substance /

substance is dragged down to some extent by the barium sulphate and is weighed as such. For probably the same reason the analytical figure for the sulphur content of calcium sulphate (20.4%) is lower than the theoretical figure (20.8% for $CaSO_4$, $2H_2O$). Consequently, the calculated figure for E.1703 must also be low, and the error due to occlusion of calcium sulphate during the precipitation of barium sulphate is not noticeable.

Additional samples were compounded with calcium compounds (Table 7) and were analysed by the Carius method. The analytical results - outlined in Table 8 - were again lower than the calculated figures.

Table 7

Mixing Number	Drug	Parts by Weight			Time of Cure in mins. @ 50 lbs. Steam
		Drug	Plantation Sheet	Sulphur	
E.1693/1	Lime	1	100	8	135
E.1693/2	Lime	4	100	8	105
E.1683/1	Whiting	50	100	8	150
E.1683/2	Whiting	25	100	8	150

Table 8 /

Table 8

Mixing Number	Calculated %age	Possible Error of calculated %age	Analytical Results (%)	Mean Analytical %age	Difference between calculated & analytical %ages
E.1693/1	7.41	±.15	7.19 7.28	7.24	-.17
E.1693/2	7.22	±.14	7.03 7.04	7.04	-.18
E.1683/1	5.12	±.10	4.96 5.03	5.00	-.12
E.1683/2	6.08	±.12	5.93 5.95	5.94	-.14

The results obtained with the mixing containing antimony sulphide were also low. A considerable excess of hydrochloric acid must be added to prevent precipitation of antimony oxychloride when the solution is diluted prior to adding barium chloride; the solubility of barium sulphate in the mother liquor is consequently increased and the low results may be partly explained thereby.

Lastly, the analytical results for the sample of vulcanite were lower than the calculated figures by more than the allowable amount. Although it has been shown in the experiments to determine the accuracy of the /

the milling and vulcanising operations that no appreciable amount of sulphur is lost during the "curing" of a "soft " rubber, the same cannot be assumed to hold good for "hard" rubbers.

In this connection, reference may be made to the recently published paper on the "Nature of Vulcanisation," Part IV, by H. P. and W. H. Stevens.[1] These workers found that at low temperatures by means of accelerators it is possible to produce vulcanite containing "combined sulphur" considerably in excess of that required for the formula C_5H_8S. "Having re- "gard to the hydrogen sulphide and other volatile "sulphur compounds evolved in appreciable quantities "during vulcanisation, it is evident that part of the " 'combined sulphur' results from substitution of "hydrogen by sulphur."

Accordingly, a sample of the uncured stock of mixing E.1705 was analysed in duplicate for total sulphur by the Carius method. The results obtained - 34.3% and 34.0% - mean 34.2% - are only a shade higher than the figures for the cured stock. Consequently, the discrepancy between the analytical and calculated values for the cured stock cannot be wholly due to loss of sulphur during vulcanisation. The

matter /

matter was not pursued further, however, since the discrepancy is not really very great.

Consideration of Methods of Estimating Total Sulphur.

These are almost without exception oxidation processes, differing only in the nature of the oxidising agent and the conditions under which it is used. Consequently, we must consider, in the first instance, methods of performing the oxidation, and, secondly, the estimation of the sulphuric acid produced.

The Oxidation.

All methods of wet oxidation involve the use of nitric acid. This substance when used alone at atmospheric pressure is not, however, a satisfactory reagent for the oxidation of vulcanised rubber. The oxidation of the sulphur is slow and the caoutchouc is not completely decomposed, some remaining in solution as nitro-compounds and complex organic acids. The filtration of the precipitate is rendered difficult by the presence of organic substances in the solution,[2] and the determination will frequently be vitiated by the precipitation of the barium salts of organic /

organic acids on the addition of barium chloride.[3] Consequently, in any method of wet oxidation, some means have to be adopted of adding to the activity of the nitric acid. Thus, in the Carius method, the activity of the nitric acid is considerably increased by the high pressure developed within the sealed tube.

Considerable attention has been bestowed upon methods which involve digestion of the rubber with nitric acid at atmospheric pressure, followed by fusion with alkali carbonates and nitrates to complete the oxidation. With regard to this method, which is due originally to Henriques,[2] it is important to note that when applied to rubbers containing either lead sulphate or barium sulphate as mineral "fillers," the whole of the sulphur is rendered soluble and included in the determination. A serious disadvantage of methods of this type is the occasional loss caused by spurting during fusion: this is attributed to the difficulty experienced in mixing the solid fusion substances with the syrupy nitric acid solution. Another weak feature is said to be the frequent breaking of crucibles during the fusion process. When, however, such accidents are avoided, the method gives results of undoubted accuracy, and, indeed, a modification, due /

due to Waters and Tuttle,[4] has been adopted as standard by the Rubber Division of the American Chemical Society. Nevertheless, all methods of this type are tedious, and numerous modifications have been devised in which the fusion process is dispensed with, thereby shortening the procedure, and at the same time avoiding the risk of losses due to spurting and breakage of crucibles.

Methods of oxidation with nitric acid at atmospheric pressure, without subsequent fusion, have been devised by Rothe,[5] Stevens,[6] Davies and Rosenstein,[7] Kratz, Flower and Coolidge,[8] Pearson,[9] Dyer and Watson,[10] and by Munro;[11] these differ from one another only in the means employed to supplement the activity of the nitric acid. In 1923, P. Dekker[12] published the results of a very thorough investigation of the estimation of sulphur in rubber, and concluded that, of all the above-mentioned wet oxidation methods in which the fusion is dispensed with, only the procedure proposed by Kratz, Flower and Coolidge was comparable in accuracy with the method of Waters and Tuttle. The method of Kratz, Flower and Coolidge consists in digesting the rubber in the first instance with a solution of zinc oxide in nitric acid and subsequently /

subsequently adding bromine and potassium nitrate to complete the oxidation. Because of its greater practicability this method is preferred by Dekker to that of Waters and Tuttle, except for the estimation of total sulphur in rubbers containing high percentages of sulphur, e.g., vulcanite, when the latter method is declared to give more satisfactory results. This newer method did not, however, lead to any considerable saving in time: the need for a more rapid procedure still remained.

Recently there has been published by E. Kahane[13] a further method of this type in which the rubber is oxidised by means of nitric and perchloric acids. The action takes place in two stages, the nitric acid first forming soluble nitro-derivatives which are then completely oxidised by the perchloric acid, giving on dilution a clear solution from which the sulphuric acid is precipitated with barium chloride in the usual way. The oxidation is stated to be complete in less than 10 minutes, and this rapidity, combined with the apparent simplicity of procedure, led to its being studied fairly fully.

In his original paper, Kahane advises the use of 10 ccs. of concentrated nitric acid and 5 ccs. of perchloric /

perchloric acid with 1 gram of rubber in a Kjeldahl flask. (In a subsequent private communication the use of fuming in place of concentrated nitric acid was advised.) Some preliminary estimations with calibrated mixings indicated that, with these proportions of acid to rubber, the oxidation of the sulphur was incomplete. When smaller quantities of rubber were used (about 0.25 gram of rubber to 15 ccs. of mixed acids) the oxidation was much more complete, but the results were still low. Several possible sources of error was then investigated in turn.

There is firstly the possibility of loss of sulphuric acid by volatilisation when the excess of nitric and perchloric acids is removed by boiling. Accordingly, approximately 0.25 gram of raw rubber was weighed out and added to a mixture of 10 ccs. of fuming nitric acid, 5 ccs. of perchloric acid, and a known weight of pure concentrated sulphuric acid. The oxidation of the rubber was then performed in the usual way and the sulphuric acid precipitated as barium sulphate and weighed. Knowing the concentration of the sulphuric acid, the percentage of sulphur in the crude rubber, and the weight of residue obtained in a blank analysis, a theoretical value for this /

this weight of barium sulphate could be obtained.

Weight of raw rubber taken	0.1643 gram
Total sulphur content of raw rubber (determined by Carius method)	0.08 %
Weight of sulphuric acid added ..	0.0540 gram
Strength of sulphuric acid (determined volumetrically and confirmed from S.G.)	98.13% (by weight)
Calculated weight of barium sulphate	0.1271 gram

Weight of precipitate obtained ..	0.1346 gram
Weight of precipitate obtained in a blank determination	0.0067 gram
Weight of barium sulphate	0.1279 gram

There is good agreement between the analytical and calculated figures. This is in concordance with the statement by H. E. Potts[14] that loss of sulphuric acid due to volatilisation on heating with nitric acid is negligible.

The second possibility is that some of the sulphur might escape as sulphur dioxide. In many methods of performing the oxidation bromine is added to prevent losses from this source. It was found that if the initial interaction of the rubber and oxidising /

oxidising acids took place over a small flame in an atmosphere of bromine, considerably improved results were obtained.

A still further possibility is loss due to mechanical removal of sulphur with the gaseous products of oxidation. H. P. Stevens[15] proved that this does take place during the action of nitric acid on vulcanised rubber, and suggested, in describing his own method, providing the flask with a suitable condenser. As a preliminary, however, a further series of analyses were performed, in each of which the long neck of the Kjeldahl flask was kept cool by means of a blast of cold air; a ring of asbestos board was placed round the neck just above the bulb for the same purpose. An atmosphere of bromine was again maintained in the flask during the initial stages of the oxidation by adding 0.5 cc. of bromine and warming gently for half-an-hour before boiling the solution. The following results were obtained

Table /

Table 9

Mixing Number	Calculated %age	Mean Analytical %age (Carius)	I. Analytical %ages ($HClO_4$ method)	I. Mean %age	II. Analytical %ages ($HClO_4$ method)	II. Mean %age
E.1681	7.48	7.36	7.38 7.31	7.35	7.34 7.31	7.33
E.1682	3.93	3.92	3.89 3.93	3.91	3.85 3.86	3.86
E.1705	35.1	34.0	33.9 34.2	34.1	33.7 33.8	33.8

"Blank" analyses had been done previously and the mean weight of residue so obtained was subtracted from the weight of barium sulphate in each of the above determinations.

Qualitative analysis indicated that the solution which remains at the conclusion of the oxidation contained a moderate amount of chlorate and a trace of nitrate. These anions lead to high results when solutions of sulphuric acid are estimated gravimetrically as barium sulphate. Accordingly, in the analyses detailed in the columns headed II. of Table 9, these acids were removed by evaporating the solution with 2 grams of pure sodium chloride prior to precipitating the sulphate with barium chloride.

Since the results obtained are in quite satisfactory /

satisfactory agreement with those obtained by the Carius method, the attachment of a condenser to the flask does not seem necessary.

Reference must be made to the recently published work of Wolesensky[16]. In a search for a rapid and accurate method for determining sulphur in rubber it was found that oxidation of the sample by means of the Parr sulphur bomb is unsatisfactory when the sulphur content of the rubber is low, because the samples that can be used for this purpose are too small for accurate results, or, if larger samples are used, the oxidation is incomplete. The use of a mixture of nitric and perchloric acids as described by Kahane was also considered unsatisfactory, but with certain modifications the method was made to yield very good results. The chief modifications recommended are the use of a more dilute solution of nitric acid, allowing the rubber to dissolve completely on the steam bath before heating more strongly, then heating to gentle boiling until oxidation is complete, and finally destroying the residual nitric acid by means of hydrochloric acid. It is pointed out that in many cases where barium and lead compounds are absent, subsequent fusion with alkali can be dispensed with. In other cases it is known that only barium is present in /

in the form of its sulphate which could readily be filtered off from the solution after the rubber had been dissolved, without interfering with the determination of the rubber-sulphur in the solution in the usual way. If the barium is present in the form of the carbonate, all of the sulphur would probably be precipitated immediately, but in many cases it could be determined with sufficient accuracy for most purposes by merely filtering off the precipitate, washing, and weighing as barium sulphate. Rubber compounds which are known to contain only lead might be handled in a similar way, with due regard for the solubility of lead sulphate. Finally, in those comparatively few cases in which a fusion is necessary, this can be done upon the precipitate which is filtered off from the acid solution obtained by oxidising the rubber compound with the mixture of nitric and perchloric acids.

In the later paper [16] it is shown that barium sulphate can be decomposed to the extent of over 99% in a single operation by boiling for 1 or 2 hours with a strong solution containing at least fifteen times the theoretical amount of sodium carbonate. Although this degree of decomposition is not so high as that attained by the fusion method and is not sufficient /

sufficient for the requirements of the most exacting quantitative analysis, it is considered sufficient for many purposes, particularly in the analysis of materials containing only small amounts of barium sulphate, besides offering the advantages of speed and simplicity of operation.

The present author has proceeded along different lines and has arrived at a somewhat different procedure. By combining this method of oxidation with a volumetric process for the estimation of sulphuric acid a fairly rapid determination has been outlined. Time has not yet been found to compare this new method with that of Wolesensky, but good results obtained throughout systematic analyses of the calibrated mixings have warranted publication of the present author's method.

The fact that nitric acid is not an entirely satisfactory reagent for the oxidation of vulcanised rubber has already been observed; a method of sulphur estimation which did not involve the use of this substance would, therefore, be very desirable, and considerable attention has consequently been bestowed on methods of dry oxidation, i.e., of oxidation by direct fusion.

The use of Eschka's fusion mixture as proposed by /

by Esch[17] and of the zinc oxide - potassium nitrate mixture suggested by Kaye and Sharp[18] are the best known of the older methods. The former is quite accurate provided an intimate mixture of the rubber particles and the fusion substances is obtained, but it is not sufficiently rapid for ordinary analytical work; while the spurting occasioned by the fusion of rubber with zinc oxide and potassium nitrate is a serious objection to the latter. Recently there has been published by V. C. Butironi[19] a method which consists in fusing the rubber with pure potassium hydroxide in a silver crucible and completing the oxidation by adding potassium nitrate in small portions; the melt is dissolved in water, acidified and boiled to remove carbon dioxide; insoluble substances are then removed by filtration and barium sulphate precipitated in the usual way. Nevertheless, the great possibility of losses from spurting will always tend to hinder the adoption of any method of oxidation by direct fusion in an open crucible, and consequently no attempt was made to test the accuracy of Butironi's method.

A method has been worked out in the laboratories of the B. F. Goodrich Co., in which use is made of the Parr sulphur bomb[20], the oxidising agent being a fusion /

fusion mixture consisting mainly of sodium peroxide with added small amounts of potassium chlorate and sugar. The recently published opinions of Wolesensky on this method have been mentioned previously. Some time ago this method was subjected to a few tests in the laboratory at Castle Mills, but was rejected on account of the frequent incompleteness of the oxidation. Recently it has been studied by P. Dekker[12], who obtained quite satisfactory results but rejected the method on account of the rapid corrosion of the walls of the bomb by the fusion mixture.

Several methods have been proposed which consist in burning the rubber in a current of oxygen, collecting the sulphur dioxide evolved in a suitable absorbent, oxidising if necessary, and estimating by the usual gravimetric means.[21] Such methods are fairly rapid but are only applicable to pure rubber-sulphur mixings since only the volatile sulphur is determined.

The Estimation of Sulphuric Acid.

Methods for this purpose are of three types - Gravimetric, Volumetric, and Turbidimetric.

Up /

Up to the present the Gravimetric has been the sole method in vogue. Theoretically, the procedure is very simple, it being only necessary to precipitate with barium chloride, filter and weigh the barium sulphate. Practically, however, it is a process fraught with many difficulties. According to the manner of precipitating the barium sulphate, the composition of the precipitate varies in such a way that sometimes the results are too high and sometimes too low. During precipitation, errors may be introduced from the following sources:-

1. Solubility of barium sulphate in the mother liquor.

The error from this source depends chiefly on the amount of free acid and is generally decreased by using excess of barium and avoiding excess of acid.

2. Occlusion of other sulphates present in solution.

All barium sulphate precipitates carry down varying quantities of the alkali sulphates, thus lowering the results. Divalent and more especially trivalent metallic ions also exert disturbing influences; a large number of observers have recorded occlusion of the sulphates of the alkaline earths, cobalt, copper, iron, aluminium, etc. The degree of occlusion depends in all cases on the concentration of the salts present /

present and on the fineness of the precipitate. Occluded salts cannot be removed by washing.

3. Loss by volatilisation during ignition of the precipitate

Barium sulphate when precipitated from alkali sulphates always occludes a certain amount of "free" sulphuric acid, probably as the acid sulphate of the alkali metal. It arises from the free acid added and increases with it, up to a point. Alkali chlorides decidedly increase its amount and when these are present in considerable concentration it becomes the chief source of error.

4. Occlusion of barium chloride. If the precipitation is performed slowly the amount of precipitant in the un-ignited precipitate is relatively small, and since all but a trace of the chlorine is eliminated as hydrochloric acid by interaction with the "free" sulphuric acid, it is not a source of error. When, however, the precipitate is very rapidly formed, the amount of barium chloride is multiplied several times and the chlorine is no longer entirely eliminated on ignition.

5. Nitrates and Chlorates. These cause occlusion of barium nitrate and barium chlorate.

It is said to be advisable to postpone filtration for at least six hours after precipitation, since the /

the freshly precipitated substance is rather more soluble than a precipitate which has stood for some time in contact with the mother liquor. Curiously enough, a precipitate of barium sulphate which has been filtered and washed immediately after precipitation is less easily freed from occluded salts by washing, and, therefore, contains more occluded salts on ignition than one which has been left to stand for some time. The increase in the size of the particles which occurs when the precipitate is allowed to stand for some time is also of considerable advantage in filtration.

It will be observed that the errors due to solubility of barium sulphate, occlusion of alkali sulphates, and volatilisation of sulphuric acid, act in opposition to those due to occlusion of barium chloride, nitrate and chlorate, and it is possible so to regulate the conditions of precipitation that a fairly accurate compensation is obtained.

In the presence of salts of the alkali metals or ammonium (nitrates and chlorates having been removed previously) a sufficiently accurate result is said to be obtained by the rapid precipitation method of Hintz and Weber[22]. The dilute sulphate solution, slightly acidified with hydrochloric acid, is heated to /

to boiling and precipitated by excess of boiling barium chloride, added all at once with continuous stirring. The solution is allowed to stand in a warm place for half-an-hour, filtered, and the precipitate washed with hot water and ignited. This method was investigated by Allen and Johnstone[23] who showed that the losses by volatilisation of sulphuric acid are, in the first place, reduced by reason of a more complete conversion of the original sulphate into barium sulphate, and, in the second place, partly compensated by an adsorption of barium chloride by the precipitate.

In the laboratories at Castle Mills, it has been the practice in the past to follow the traditional method of slow precipitation, and, as it was within the scope of this work to indicate what inaccuracies this might lead to, it was decided to retain this procedure in the calibration analyses. The details have been given previously and the results discussed.

Many Volumetric processes for the estimation of sulphuric acid have been advanced from time to time, but, of these, only the benzidine method due to Raschig[24] has been studied in this investigation. This method is based on the fact that benzidine reacts with /

with sulphuric acid to form benzidine sulphate which is very sparingly soluble both in water and in alcohol. Benzidine itself is a very weak base - neutral to phenolphthalein; consequently, aqueous solutions of its salts undergo hydrolysis, and the acid radical can be titrated directly with standard alkali. Raschig recommends treating the neutral or faintly acid solution of the sulphate with a solution of benzidine hydrochloride, filtering off the precipitated benzidine sulphate, which is then washed, suspended in water and titrated with standard sodium hydroxide at 50°C. The more important sources of error are:-

1. Slight solubility of benzidine sulphate in water,
2. Slight adsorption of benzidine hydrochloride by the precipitate,
3. Imperfect titration due to the "balling" of the precipitate when it is overdried,
4. Incomplete precipitation of sulphate through using insufficient excess of benzidine hydrochloride,
5. The need for slight excess of the sodium hydroxide solution owing to adsorption of the indicator by the paper pulp.

Some of these errors compensate one another - others can obviously be avoided with practice.

Friedheim and Nydegger[25] conducted a thorough examination of the utility of this method for the estimation of sulphur in pyrites, and concluded that the most accurate determinations could be made with solutions /

solutions containing 0.1 - 0.2% of sulphuric acid. They state that, contrary to Raschig's procedure, it is preferable to pour the solution of benzidine hydrochloride into the sulphate solution, whereas Vlastimil and Matula[26] consider Raschig's method of precipitation more accurate. The solubility of the precipitate in the mother liquor and in water or alcohol increases considerably with rise in temperature; accordingly, Christie and Bisson[27] wash with the minimum amount of cold water, whereas Vlastimil and Matula state that it is preferable to wash with 24% alcohol owing to the diminished solubility of benzidine sulphate.

If ferric iron be present, some will be occluded by the precipitate; if, however, the ferric iron be first reduced to the ferrous condition, the interference is lessened considerably.

A solution of benzidine hydrochloride was prepared according to Raschig's prescription, viz:-

Triturate 40 grams of pure benzidine with 40 ccs. of water and rinse the paste into a litre-graduated flask with about 750 ccs. of water. Add 50 ccs. of concentrated hydrochloric acid and dilute to the mark. Shake well. Soon the benzidine will all dissolve, forming a brown liquid which may be filtered if necessary /

necessary. Brown flakes may separate from the solution on long standing: these do no particular harm. When using as a reagent, dilute with nineteen times as much water.

A series of preliminary analyses by the benzidine method on samples of a carefully standardised solution of sulphuric acid led to the following conclusions. At a concentration of 0.1% of sulphuric acid the method is one of considerable accuracy. Addition of the sulphuric acid solution to the solution of benzidine hydrochloride possesses no particular advantage over the normal method of precipitation advocated by Friedheim and Nydegger. Washing with 24% alcohol is to be preferred to washing with water.

Sulphate solutions containing approximately 0.1% of sulphate (calculated as H_2SO_4) were prepared from the sulphates of sodium, magnesium, calcium and zinc, and from iron alum; each of these solutions was standardised by gravimetric determinations. Estimations were then made with each by the benzidine method. In each case 25 ccs. of the sulphate solution were precipitated with 50 ccs. of the diluted benzidine hydrochloride solution; after 10 minutes, the benzidine sulphate was filtered through a double filter paper pressed on to a Witt's filter plate, the precipitate was /

was washed on the filter with 15 ccs. of 24% alcohol; the filter paper and contents were then transferred to a conical flask, shaken up into a "slurry" with distilled water and titrated at 50°C. with $\frac{N}{50}$ sodium hydroxide.

Table 10 /

Table 10

Number of Analysis	Solute	Concentration of solution in gms/litre	Theoretical figure for weight of H_2SO_4 in gms. present in 25 ccs.	Gravimetric figure for weight of H_2SO_4 in gms. present in 25 ccs.	Volumetric figure for weight of H_2SO_4 in gms. present in 25 ccs.
1	$Fe(NH_4)(SO_4)_2$, $12H_2O$	2.3590	.0240	.0235	.0234
2					.0235
x 3	$Fe(NH_4)(SO_4)_2$, $12H_2O$	2.3590	.0240	.0235	.0241
x 4					.0242
5	Na_2SO_4, $10H_2O$	3.2540	.0248	.0247	.0252
6					.0253
7	$MgSO_4$, $7H_2O$	2.4130	.0240	.0240	.0237
8					.0236
9	$CaSO_4$, $2H_2O$	1.6660	.0237	.0233	.0240
10					.0239
11	$ZnSO_4$, $7H_2O$	2.8150	.0240	.0242	.0241
12					.0243

x 10 ccs. of a 5% solution of hydroxylamine hydrochloride were added to reduce ferric iron to ferrous before precipitating the sulphate.

As will be seen from Table 10, very good agreement was obtained in these preliminary analyses between gravimetric and volumetric results, and steps were immediately taken to determine whether this volumetric procedure would be suitable for use in rubber analysis in conjunction with the method of oxidation by means of nitric acid, perchloric acid and bromine. A perusal of the literature revealed the fact that chloric acid, which is produced by reduction of perchloric acid during the oxidation, reacts with benzidine in presence of sulphuric acid, giving a characteristic yellow coloration[28]. Qualitative experiments indicated that previous reduction of the chloric acid with zinc or with hydroxylamine hydrochloride inhibited this reaction. Quantitative estimation, however, showed that better results are obtained when the reduction is performed with hydroxylamine hydrochloride, the residual solution neutralised with ammonia and then made faintly acid with $\frac{N}{10}$ hydrochloric acid, prior to precipitation of benzidine sulphate. The figures and details of these experiments are summarised in Tables 11, 12, 13 and 14.

Table 11 /

Table 11

In each case, 2 ccs. of 60% perchloric acid were added to 10 ccs. of the solution of sulphuric acid; 0.2 gram of zinc dust was then stirred in and the mixture heated for 15 minutes on the hot plate. The residual zinc was filtered off, and the volume of the filtrate made up to 250 ccs. before precipitation with benzidine hydrochloride. The results are:-

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	100	300	9.00	8.94	-10.6
2	150	500	9.34	9.28	- 7.2
3	200	700	9.67	9.60	- 4.0
4	250	900	9.87	9.79	- 2.1
5	300	1100	9.95	9.87	- 1.3

Table 12

The conditions differed from those outlined under Table 11 only in that the filtrate from residual zinc was made faintly alkaline with ammonia and then just acid to methyl red with N/10 hydrochloric acid, prior to the precipitation of benzidine sulphate. The results are appended:-

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	100	300	9.29	9.24	-7.4
2	150	500	9.53	9.47	-5.2
3	200	700	9.76	9.68	-3.2
4	250	900	9.92	9.84	-1.6
5	300	1100	9.98	9.90	-1.0

Table 13

In each case 10 ccs. of a 5% solution of hydroxylamine hydrochloride were added to 10 ccs. of the sulphuric acid. The solution was then diluted to 250 ccs. and the sulphate precipitated. The following are the results obtained:-

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	100	300	9.02	8.96	-10.4
2	150	500	9.52	9.45	- 5.5
3	200	700	9.86	9.80	- 2.0
4	250	900	9.95	9.87	- 1.3
5	300	1100	9.99	9.91	- 0.9

Table 14

The procedure differed from that under Table 13 only in that, after the addition of hydroxylamine hydrochloride, the solution was first made faintly alkaline with ammonia and then faintly acid with N/10 hydrochloric acid prior to dilution and precipitation of benzidine sulphate. The following results were obtained:-

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	100	300	9.35	9.28	-7.2
2	150	500	9.68	9.61	-3.9
3	200	700	9.98	9.89	-1.1
4	250	900	10.02	9.94	-0.6
5	300	1100	10.06	9.98	-0.2

Friedheim /

Friedheim and Nydegger's conclusion that the most suitable concentrations for use with this method are 0.1% - 0.2% of sulphuric acid has already been referred to. Such concentrations are considerably higher than those encountered in rubber analysis and the excess of precipitant necessary for the accurate estimation of these dilute solutions had, therefore, to be determined. A considerable number of determinations were performed at various likely dilutions with measured volumes of carefully standardised solutions of sulphuric acid to which had been added definite amounts of perchloric acid, which, of course, contains traces of chloric acid. At each dilution various excesses of precipitant were used and the estimations performed in the usual manner.

The estimation of very dilute solutions of sulphuric acid (approximately 0.01%) was first studied by adding increasing excesses of precipitant to 10 cc. portions of .0542-N sulphuric acid diluted to 250 ccs. In each experiment 2 ccs. of perchloric acid were added to the sulphuric acid before dilution; chloric acid was reduced by means of hydroxylamine hydrochloride and the solution was made just acid to methyl red before dilution and precipitation of benzidine sulphate. The results obtained are detailed in Table 15 /

Table 15.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	30	20	7.47	7.42	-25.8
2	40	60	8.84	8.78	-11.2
3	60	140	9.37	9.30	- 7.0
4	80	220	9.59	9.52	- 4.8
5	100	300	9.88	9.81	- 1.9
6	120	380	9.97	9.90	- 1.0
7	140	460	9.96	9.89	- 1.1
8	160	540	9.98	9.91	- 0.9
9	180	620	10.01	9.94	- 0.6
10	200	700	10.03	9.96	- 0.4
11	220	780	10.03	9.96	- 0.4
12	240	860	10.05	9.98	- 0.2
13	260	940	10.04	9.97	- 0.3
14	280	1020	10.07	9.99	- 0.1
15	300	1100	10.06	9.98	- 0.2
16	320	1180	10.07	9.99	- 0.1
17	340	1260	10.10	10.02	+ 0.2
18	360	1340	10.09	10.01	+ 0.1

Solutions of sulphuric acid corresponding to those to be obtained from the oxidation of mixings containing 4% of sulphur were estimated at various dilutions with varying excesses of precipitant. The results are detailed in Tables 16, 17 and 18. In each case perchloric acid was present, chloric acid was reduced with hydroxylamine hydrochloride, and the solution was neutralised before precipitation.

Table /

Table 16.

In each case 11.5 ccs. of .0542-N sulphuric acid were diluted to 30 ccs. before precipitation.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	30	0	7.92	7.86	-31.7
2	60	100	9.80	9.73	-15.4
3	90	200	11.16	11.08	- 3.7
4	120	300	11.36	11.28	- 1.9
5	150	400	11.56	11.48	- 0.1
6	180	500	11.53	11.45	- 0.3
7	210	600	11.57	11.49	- 0.1
8	240	700	11.51	11.44	- 0.3
9	300	900	11.57	11.49	- 0.1
10	360	1100	11.57	11.49	- 0.1

Table 17.

In each case 11.5 ccs. of .0542-N sulphuric acid were used and the final volume of the solution prior to precipitation of benzidine sulphate was 60 ccs.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	30	0	7.16	7.10	-38.3
2	60	100	8.89	8.82	-23.3
3	90	200	9.54	9.47	-17.7
4	120	300	10.26	10.19	-11.4
5	150	400	10.59	10.51	- 8.6
6	180	500	11.06	10.98	- 4.5
7	210	600	11.40	11.32	- 1.6
8	240	700	11.60	11.51	+ 0.1
9	270	800	11.57	11.48	- 0.1
10	300	900	11.63	11.54	+ 0.3
11	360	1100	11.56	11.49	- 0.1
12	420	1300	11.58	11.50	0

Table 18.

In each case 11.5 ccs. of 0.0542-N sulphuric acid were used and the final dilution was 120 ccs. prior to precipitation of benzidine sulphate.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0542-N H_2SO_4 (ccs.)	%age Error
1	120	300	9.70	9.63	-16.8
2	150	400	10.30	10.22	-11.1
3	180	500	10.82	10.73	- 6.7
4	210	600	11.31	11.23	- 2.4
5	240	700	11.55	11.46	- 0.6
6	270	800	11.61	11.52	+ 0.2
7	300	900	11.60	11.51	+ 0.1
8	330	1000	11.57	11.48	- 0.1
9	360	1100	11.58	11.50	0
10	390	1200	11.60	11.51	+ 0.1
11	420	1300	11.59	11.50	0
12	450	1400	11.60	11.51	+ 0.1

Solutions corresponding to 8% and 16% mixings were similarly studied at a dilution of 120 ccs., the procedure being analogous to that already described. The results are given in Tables 19 and 20.

Table /

Table 19.

In each case the volume of .0491-N sulphuric acid used was 25.5 ccs. - corresponding approximately to the sulphuric acid obtainable from 0.25 gram of an 8% mixing.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0491-N H_2SO_4 (ccs.)	%age Error
1	60	0	22.95	25.15	- 1.4
2	90	50	23.04	25.24	- 1.0
3	120	100	23.12	25.33	- 0.7
4	150	150	23.19	25.41	- 0.3
5	180	200	23.26	25.49	0
6	210	250	23.30	25.53	+ 0.1
7	240	300	23.31	25.53	+ 0.1
8	270	350	23.24	25.47	- 0.1
9	300	400	23.29	25.51	0
10	330	450	23.22	25.47	- 0.1
11	360	500	23.32	25.55	+ 0.2
12	390	550	23.31	25.53	+ 0.1
13	420	600	23.30	25.52	+ 0.1
14	450	650	23.23	25.47	- 0.1

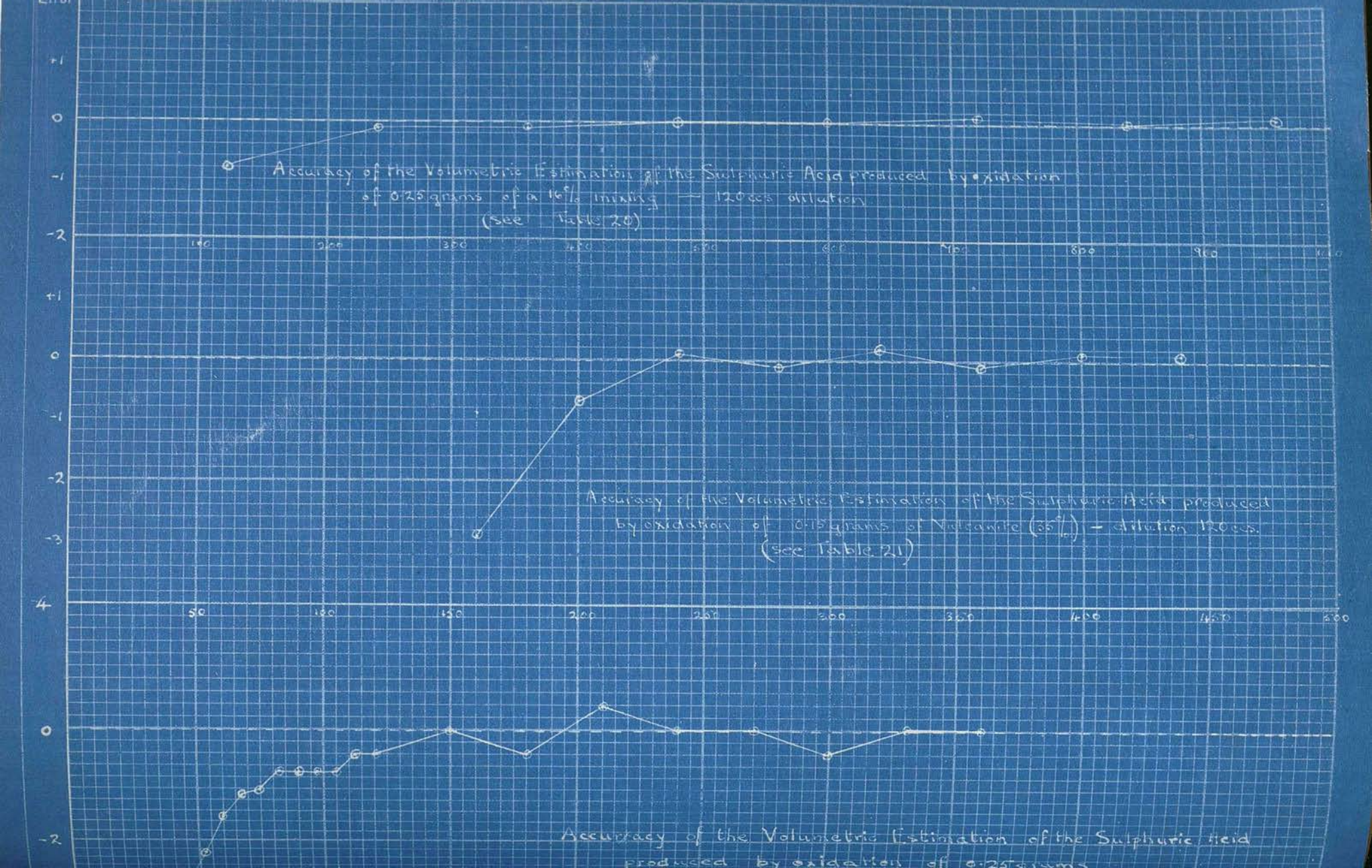
Error
+1
0
-1
-2
100
200
300
400
600
800
960
Accuracy of the Volumetric Estimation of the Sulphuric Acid produced by oxidation of 0·25 grams of a 16% mixture — 120 ccs dilution
(See Table 20)
+1
0
-1
-2
-3
50
100
150
200
250
300
350
400
450
500
Accuracy of the Volumetric Estimation of the Sulphuric Acid produced by oxidation of 0·15 grams of Vulcanite (35%) — dilution 120 ccs.
(See Table 21)
4
0
-2
Accuracy of the Volumetric Estimation of the Sulphuric Acid produced by oxidation of 0·25 grams

Table 20.

In each case 51.0 ccs. of .0491-N sulphuric acid were used.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0491-N H_2SO_4 (ccs.)	%age Error
1	120	0	46.18	50.59	- 0.8
2	240	100	46.49	50.95	- 0.1
3	360	200	46.51	50.97	- 0.1
4	480	300	46.56	51.02	0
5	600	400	46.53	51.00	0
6	720	500	46.57	51.04	+ 0.1
7	840	600	46.54	51.00	0
8	960	700	46.58	51.04	+ 0.1

Oxidation of 0.15 gram of a vulcanite (35% of sulphur) will yield 0.1606 gram of sulphuric acid - the amount present in 55.6 ccs. of .0589-N acid (approximately). This volume was used in each analysis, the dilution prior to precipitation of benzidine sulphate being 120 ccs. Here again, perchloric acid was present, and the usual procedure was adopted for the reduction of chloric acid and the neutralisation of the solution. The results are given in Table 21.

Table /

Table 21.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .0538-N NaOH (ccs.)	Equivalent volume of .0589-N H_2SO_4 (ccs.)	%age Error
1	160	0	59.08	53.98	- 2.9
2	200	25	60.46	55.22	- 0.7
3	240	50	60.96	55.68	+ 0.1
4	280	75	60.81	55.53	- 0.1
5	320	100	61.06	55.73	+ 0.2
6	360	125	60.79	55.52	- 0.1
7	400	150	60.94	55.66	+ 0.1
8	440	175	60.92	55.64	+ 0.1

Owing to the wide-spread use of accelerators of vulcanisation, most modern commercial rubber mixings contain considerably less than 4% of sulphur. Oxidation of 0.25 gram of a rubber mixing containing 1% of sulphur would yield 0.0077 gram of sulphuric acid which is approximately contained in 2.65 ccs. of .0589-N acid. Portions of this volume were estimated at a dilution of 120 ccs. with increasing excesses of precipitant.

Table /

Table 22.

No. of Experiment	Volume of precipitant used (ccs.)	%age excess of precipitant	Titration of .01075-N NaOH (ccs.)	Equivalent volume of .0589-N H_2SO_4 (ccs.)	%age Error
1	7.5	0	10.20	1.86	- 29.7
2	15.0	100	12.65	2.31	- 12.8
3	22.5	200	13.45	2.46	- 7.2
4	30.0	300	13.84	2.53	- 4.5
5	37.5	400	14.01	2.55	- 3.8
6	45.0	500	14.09	2.57	- 3.0
7	52.5	600	14.20	2.59	- 2.3
8	60.0	700	14.25	2.60	- 1.5
9	67.5	800	14.36	2.62	- 1.1
10	75.0	900	14.37	2.62	- 1.1
11	82.5	1000	14.40	2.63	- 0.7
12	90.0	1100	14.41	2.63	- 0.7
13	97.5	1200	14.39	2.63	- 0.7
14	105.0	1300	14.40	2.63	- 0.7
15	112.5	1400	14.45	2.64	- 0.4
16	120.0	1500	14.47	2.64	- 0.4
17	150.0	1900	14.50	2.65	0
18	180.0	2300	14.47	2.64	- 0.4
19	210.0	2700	14.54	2.66	+ 0.4
20	240.0	3100	14.51	2.65	0
21	270.0	3500	14.49	2.65	0
22	300.0	3900	14.47	2.64	- 0.4
23	330.0	4300	14.48	2.65	0
24	360.0	4700	14.50	2.65	0

The accompanying graphs summarise the results detailed in the foregoing tables. It will be observed from the curves for "%age error" against "volume of precipitant used" that for any concentration of sulphuric acid likely to be encountered in /

Accuracy of the Volumetric Estimation of the Sulphuric Acid produced by oxidation of precipitations of the Sulphide (Gee Table 18).

Accuracy of the Volumetric Estimation of the Sulphuric Acid produced by oxidation of the Sulphide Precipitations of the Chlorides (See Table 19).

in rubber analysis, sufficiently accurate estimations can be made, after reducing the chloric acid with hydroxylamine hydrochloride and rendering the solution faintly acid by means of ammonia and decinormal hydrochloric acid, by diluting to 120 ccs. and precipitating with 300 ccs. of the diluted solution of benzidine hydrochloride.

One further difficulty had, however, to be surmounted. Methyl red is the most suitable indicator to use in the neutralisation of acids with ammonia, but its presence in the faintly acid solutions from which benzidine sulphate is precipitated is a distinct disadvantage; the precipitate adsorbs some methyl red and this colour interferes with the subsequent titration when phenolphthalein is the indicator. It was also noticed that the precipitates tended to darken in colour on standing in contact with the mother-liquor, probably because of oxidation of benzidine hydrochloride by the "free" perchloric acid.

Accordingly, in the application of this volumetric procedure in conjunction with the new perchloric acid procedure to the analysis of rubber samples, the perchloric acid was removed as the sparingly soluble potassium salt by adding excess of potassium hydroxide.

Perfectly /

Perfectly white precipitates were then obtained.

The last method of estimating sulphuric acid to be considered is the Turbidimetric. It has been suggested that a rapid determination of sulphate might be possible by comparing the turbidity of a solution containing a known amount of barium sulphate in suspension with that produced by the addition of barium chloride to the given solution. A considerable number of experiments were carried out in this connection using the Klett nephelometer. Suspensions of barium sulphate in water were studied at many dilutions with and without added protective colloids, but the results were far from satisfactory. Under no set of conditions could a smooth calibration curve be obtained, and in many cases it was difficult to duplicate results, even when considerable pains were taken to control governing conditions. The system would seem to react greatly to very slight changes in these conditions. This excessive sensitivity renders futile the employment of such methods for the estimation of sulphates in the complex solutions obtained by the oxidation of rubber, and the matter was therefore abandoned.

Systematic /

Systematic Analyses by the New Procedure.

The calibrated standard mixings were finally analysed for total sulphur by the following method:-

10 ccs. of fuming nitric acid (S.G. 1.50), 5 ccs. of perchloric acid (S.G. 1.54), and 0.5 cc. of bromine are introduced into a Jena Kjeldahl flask of 300 ccs. capacity. Approximately 0.25 gram of soft rubber or 0.15 gram of vulcanite are weighed out in a small glass tube of known weight; the tube and its contents are slid gently down the neck of a Kjeldahl flask into the oxidising mixture. The flask is then clamped up in a sloping position with a current of cold air impinging on the neck; a ring-shaped piece of asbestos board is placed round the top of the bulb and a closed glass bulb is placed in the mouth of the flask. The flask is gently warmed to start the oxidation which thereafter proceeds spontaneously. If a small flame be kept under the flask for half-an-hour or so, the nitration will be completed and a yellow solution of nitro-rubber will remain, in which are floating globules of free sulphur. The heating is then increased to produce gentle boiling, fumes of nitric acid being evolved. When the removal of nitric acid is /

is almost complete, the atmosphere within the flask clears and the boiling mass darkens rapidly. Thereafter the evolution of gas becomes more violent and the flame is taken away. The contents of the flask then become clear and in a few minutes are practically colourless. If the liquid does not clear during the heating, it is necessary, after cooling, to add 1 - 2 ccs. of perchloric acid and heat again to boiling, when the liquid immediately loses colour.

The residue in the Kjeldahl flask is diluted to 25 ccs. with distilled water and transferred to a 400 cc. beaker; the flask is rinsed out with two successive 25 cc. portions of distilled water and the washings added to the main solution. A solution of potassium hydroxide (4 normal) is now run in from a burette until no more potassium perchlorate is precipitated; a few drops of phenolphthalein are added and the addition of potassium hydroxide continued until the solution is alkaline. The mixed precipitate of insoluble "fillers," metallic hydroxides, and potassium perchlorate is then removed by filtering through a 15 cm. paper into a 300 cc. conical flask. 10 ccs. of a 5% solution of hydroxylamine hydrochloride are then added to the combined filtrate and washings. A decinormal solution of hydrochloric acid is then run /

run in from a burette until acidity is indicated and the solution is heated to boiling. Owing to the introduction of carbonate with the potassium hydroxide, the escape of carbon dioxide on boiling will cause the pink colour of the indicator to disappear. The addition of hydrochloric acid is continued thereafter until all the carbon dioxide has been driven off and the solution is distinctly acid. A considerable saving in time is effected at this point if the potassium perchlorate has been precipitated by carbonate-free potassium hydroxide.[x] The flask is cooled under the tap and its contents transferred to an 800 cc. beaker; the total volume at this stage should not exceed 120 ccs. 300 ccs. of the diluted solution of benzidine hydrochloride are now poured in with constant stirring and the mixture set aside for five minutes.

The /

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x This solution can be readily prepared by dissolving the requisite amount of A.R. potassium hydroxide in the minimum quantity of distilled water, adding a few grams of freshly ignited calcium carbonate and setting aside for a few days. The clear supernatant liquor is then siphoned off and brought to the necessary dilution with freshly-boiled distilled water.

The precipitated benzidine sulphate is filtered off under gentle suction through two filter papers (9 cms. diameter), pressed on to a Witt's filter plate (5 cms. diameter), and washed with the minimum quantity of 24% alcohol, added in small quantities. The filter papers and precipitate are transferred to a 250 cc. conical flask provided with a one-holed rubber stopper through which passes a tightly fitting glass rod reaching nearly to the bottom of the flask. The flask is then shaken vigorously so as to form a kind of "slurry", - precipitate, filter paper and water - quite free from lumps of benzidine sulphate. The stopper and glass rod are removed from the flask and any adhering particles of the sulphate washed back. About 2 ccs. of phenolphthalein are then added, the mixture is warmed to 50°C. on the water-bath, and titrated with $\frac{N}{20}$ sodium hydroxide until the pink colour of the indicator appears. The flask is then heated on a sand-bath until the colour has disappeared and the titration continued until a faint pink colour reappears. Boil the mixture to expel carbon dioxide and finish the titration. The end-point is indicated by the appearance of a faint pink colour in the liquid; an intense red colouration shows /

shows over-titration. At the end of the titration one or two drops of $\frac{N}{20}$ hydrochloric acid should remove the colour and this should not reappear after boiling for two minutes.

"Blank" estimations must be performed and the mean titration from a series should be subtracted throughout.

The benzidine method has been utilised by Vlastimil and Matula[26] for the estimation of sulphates in presence of lead. Satisfactory results were obtained in the analysis of lead sulphate by dissolving the sample in ammonium acetate, pouring the solution into excess of dilute benzidine hydrochloride solution, filtering, washing the precipitate with very little 24% alcohol, and titrating the benzidine sulphate with standard alkali in presence of phenolphthalein. Consequently, in the estimation of total sulphur in mixings containing litharge, the insoluble lead sulphate remaining after the oxidation is filtered off and the sulphuric acid in the filtrate is estimated as benzidine sulphate in the usual way. The precipitate of lead sulphate is dissolved from the filter in a boiling solution of ammonium acetate and the sulphate in this filtrate is also determined as benzidine /

benzidine sulphate.

In the analysis of the mixing containing ferric oxide, the ferric iron is reduced to ferrous by the hydroxylamine hydrochloride added prior to precipitating benzidine sulphate.

The results of these analyses are given in Table 23. Many of the titrations had to be performed after dark, and the use of a "Daylight Lamp" was of considerable service on these occasions.

Table 23 /

Table 23.

Mixing Number	Filler	Mean Carius Result %	Analytical Percentages (New Method)	Mean Percentages (New Method)
E.1681	--	7.36	7.33 7.39	7.36
E.1682	Zinc oxide	3.92	3.90 3.87	3.89
E.1683	Whiting	3.71	3.82 3.75	3.79
E.1684	Barytes	4.05	4.02 3.97	4.00
E.1685	Lithopone	8.29	8.18 8.21	8.20
E.1686	Carbon Black	3.70	3.74 3.70	3.72
E.1687	China Clay	3.59	3.59 3.64	3.62
E.1688	Hydrocarbon	6.98	6.91 6.99	6.95
E.1689	Magnesia	5.94	5.88 5.81	5.85
E.1690	Red Oxide of Iron	6.46	6.58 6.47	6.53
E.1691	Ultramarine	7.61	7.59 7.68	7.64
E.1692	Antimony Sulphide	8.68	8.80 8.89	8.85
E.1693	Lime	7.04	7.22 7.25	7.24
E.1694 /				

Table 23 (Contd.)

Mixing Number	Filler	Mean Carius Result %	Analytical Percentages (New Method)	Mean Percentages (New Method)
E.1694	Litharge	3.99	4.05 3.97	4.01
E.1694/1	do.	6.29	6.36 6.38	6.37
E.1695	Magnesia	7.30	7.25 7.20	7.23
E.1703	Calcium Sulphate	13.56	13.59 13.69	13.64
E.1704	Silica	3.69	3.70 3.63	3.67
E.1705	--	34.0	34.1 34.2	34.2
E.1706	Lime + Whiting	19.6	19.6 19.7	19.7
E.1713	French Chalk	3.67	3.75 3.69	3.72
E.1730	White Factice	7.54	7.53 7.58	7.56
E.1731	Brown Factice	9.00	9.10 9.01	9.06

The results throughout are in good agreement with those obtained by the Carius method, and it is of interest /

interest to note that the new procedure gave better figures for the mixings containing calcium, antimony and iron compounds than did the older method. The new method has the additional advantage of rapidity - an estimation of total sulphur can now be completed in duplicate in less than four hours.

Any review of this subject of sulphur estimation in rubber would be incomplete without reference to the gaseous reduction method for the estimation of sulphur in organic compounds devised by Ter Meulen[30], which is stated to give good results with rubber. This procedure differs in principle from any of those considered so far. The sample is mixed with an equal weight of borax and gently heated in a slow current of hydrogen. The gases evolved are passed over platinised asbestos and the sulphuretted hydrogen is absorbed by alkali and estimated iodometrically, or, if the amount present be small, by a colorimetric method using a solution of sodium plumbite. Dekker[12] performed a series of parallel analyses by this method and that of Kratz, Flower and Coolidge with very satisfactory results. The method has, however, two disadvantages, viz:-

1. /

1. Great carefulness and high analytical skill are required; the method is therefore unsuited for use in a rubber laboratory as a routine determination to be applied by an untrained staff.

2. In consequence of crystallisation phenomena affecting the free sulphur, the distribution of sulphur throughout a piece of vulcanised rubber is frequently so heterogeneous that very great differences would be found between the very small samples employed (about 10 m.grms.). Thus, four separate determinations by Dekker of the total sulphur in an under-cured mixing gave widely divergent results with this method. That the divergence is imputable solely to the heterogeneous distribution of the free sulphur throughout the samples was proved by the figures for combined sulphur by this method on samples of the same gum showing good agreement.

These disadvantages prevent the employment of the method for routine purposes, but it is of especial value for the estimation of sulphur in well cured rubbers of which only small samples are available.

Free Sulphur.

Free Sulphur.

The term "free sulphur" is generally used to denote the total amount of sulphur extracted by boiling acetone. Kelly[31] calls attention to the fact that the acetone extract includes, in addition to the sulphur which may be said to be available for further vulcanisation, small quantities of sulphur in combination with resins, proteins, rubber substitutes, etc., in the form of acetone soluble substances, and states that the total amount of such combined sulphur in the acetone extract is not a negligible quantity in an accurate free sulphur determination. Without questioning the force of Kelly's argument, mention must be made of the fact that the data which he presents cover only one compound, and it does seem as though more information were needed to show what variations exist between the free sulphur as at present determined and the amount he calls the true free sulphur. Accordingly in the present investigation the extent to which the so-called free sulphur is really uncombined has not been taken into consideration.

There are two distinct stages in the determination, viz:- extraction of the sample with acetone, and /

and then estimation of the sulphur content of the dried extract.

The Extraction.

The literature concerning the extraction is somewhat conflicting. It is universally agreed that the uncombined sulphur is much more readily soluble in boiling acetone than are the resins, proteins, etc., but there is considerable divergence as to the necessary time of extraction. Thus, L. E. Weber[32] states that for ordinary technical purposes an 8 hour period is entirely satisfactory except in the case of hard rubbers which should be extracted for 72 hours, since the free sulphur is present in a form which dissolves in acetone only with difficulty. Tuttle[4], on the other hand, states that the free sulphur is all extracted within the first four hours.

The temperature at which the extract is dried is also an important factor, and a temperature lower than 90°C. is often recommended to avoid loss of sulphur by volatilisation.

The Estimation of Sulphur in the Extract.

The following is the method at present in use in the /

the laboratories at Castle Mills for the determination of free sulphur:-

Approximately 1 gram of the finely divided sample is extracted continuously with acetone for 6 hours; the acetone solution is transferred from the extraction flask to a small CO_2 flask, the solvent removed by distillation on the steam-bath, and the flask and contents dried at 90°C. The dried extract is treated with 5 ccs. of concentrated nitric acid and 0.5 cc. of bromine, and the mouth of the flask is covered with a watch-glass. The flask is then left to stand on the side of the steam-bath for 2 hours, and is finally heated on the bath for a further period of 2 hours. The watch-glass is then removed, 1 gram of pure sodium chloride is added, and the contents of the flask evaporated to dryness. The residue is moistened with a few ccs. of concentrated hydrochloric acid and again evaporated to dryness. The contents of the flask are then taken up with a few drops of concentrated hydrochloric acid and 50 ccs. of boiling distilled water, filtered into a 400 cc. beaker and diluted to approximately 200 ccs. The liquid is then heated to boiling and barium sulphate precipitated by running in, drop by drop, 5 ccs. of a hot normal /

normal solution of barium chloride. The mixture is set aside for at least 6 hours and the estimation concluded in the usual manner, the proper precautions being taken to prevent reduction of barium sulphate during the ignition.

This procedure yields very accurate results but is tedious, and the need for a more rapid method has long been recognised.

Following upon the comparison by Dekker[33] of a number of methods of estimating free sulphur, the Netherlands Government Institute (Delft) adopted a method involving oxidation with concentrated nitric acid alone, the oxidised sulphur being thereafter precipitated as barium sulphate. If the percentage of free sulphur is above 1%, oxidation by this means is incomplete, part of the sulphur remaining as small globules. This may be dried and weighed as such. Although long practice had shown that this method gives good results, the need was felt for a method whereby all the sulphur would be oxidised. In his subsequent paper[12] Dekker concludes from a study of three newer methods, viz., the permanganate method of Dyer and Watson[10], the magnesium oxide-bromine-nitric acid method approved by the Verband Deutscher Electrochemiker /

Electrochemiker[34], and the bromine method of the Rubber Division of the American Chemical Society[4], that preference must be given to the last-named procedure. Briefly, this method is as follows:-

To the acetone extract 50-60 ccs. of distilled water and 2-3 ccs. of bromine are added, and the flask is covered with a watch glass. (If the acetone extract indicates a large amount of free sulphur the amount of bromine used may be increased.) The flask is allowed to stand for from half-an-hour to an hour on the side of the steam-bath, and the bromine is then removed by boiling. When the solution is practically colourless it is filtered into a small beaker, the beaker is covered and the contents heated to boiling. 10 ccs. of a 10% solution of barium chloride are added and after standing overnight, the barium sulphate is determined as usual.

Oxidation by this method does not, however, lead to complete destruction of the organic constituents of the extract - there always remains a very considerable residue of undissolved resin-like substances. Tuttle[4] states that a great many checks have been run by taking the insoluble residue, fusing it with sodium carbonate and potassium nitrate, and determining /

determining the sulphur as is done in the Waters and Tuttle method, but the sulphur in this residue has never exceeded 0.01% to 0.02%. It occurred to the present author that a more complete solution of the entire extract might be effected with the aid of perchloric acid.

As a preliminary, vulcanised samples were prepared according to the mixings and times of cure outlined in Table 24, the steam pressure in each case being 60 lbs.

Table 24.

Mixing Number	Parts by Weight: Plantation Sheet	Parts by Weight: Sulphur	Time of Cure in minutes
E.1681/1	100	3	150
E.1681/2	100	3	180
E.1681/3	100	3	210
E.1705/1	100	30	150
E.1705/2	100	30	180
E.1705/3	100	30	210

Following extraction of 1 gram samples of E.1681/1 for 6 hours with acetone, duplicate estimations of free sulphur by the nitric acid-bromine method now in use in the Castle Mills laboratories yielded the figures 0.65% and 0.66% - average 0.66%.

The /

The samples were weighed before and after extraction, the average percentage of extract being 2.5%.

? is this accurate

Duplicate determinations were then run by the bromine method of the Rubber Division of the American Chemical Society, using 2 gram samples of E.1681/1 with varying times of extraction. Again the amount extracted was estimated by re-weighing the samples after extraction. Blank analyses showed that it was necessary to allow for sulphur contained in the reagents. The results obtained are detailed in Table 25.

Table 25.

Time of Extraction in hours	Average percentage extract	Analytical percentages free sulphur	Mean percentage free sulphur
4	2.3	0.58 0.59	0.59
5	2.4	0.62 0.62	0.62
6	2.6	0.63 0.63	0.63
24	2.7	0.64 0.64	0.64

In the next place estimations with varying times of /

of extraction were made with samples of E.1681/1 by the following method:-

Portions of 2 grams were extracted with acetone. In each case the amount of the extract was estimated by re-weighing after extraction. The acetone solution was transferred to a Kjeldahl flask and the solvent removed by distillation. The extract was dried at 90°C. and covered with 10 ccs. of fuming nitric acid, 5 ccs. of 60% perchloric acid and 0.5 cc. of bromine. This mixture was heated over a small flame for 15 minutes - the neck of the flask being kept cool by means of a piece of asbestos over the bulb and a jet of cold air. The flame was then increased and the liquid allowed to boil gently for one minute. After the solution so obtained had cooled somewhat, it was transferred to an evaporating basin, the flask was washed out with distilled water and the washings added to the main bulk of the solution. 2 grams of pure sodium chloride were stirred in and the liquid evaporated to dryness. 10 ccs. of concentrated hydrochloric acid were then added and the liquid again brought to dryness. The residue was taken up with 2 ccs. of concentrated hydrochloric acid and about 50 ccs. of boiling distilled water, filtered, diluted to /

to about 250 ccs., heated to boiling, and barium sulphate precipitated by running in slowly, drop by drop, 10 ccs. of a hot normal solution of barium chloride. After standing overnight the barium sulphate was estimated in the usual manner. The results outlined in Table 26 have been corrected for the sulphur present in the reagents.

Table 26.

Time of Extraction in hours	Average percentage extract	Analytical percentages free sulphur	Mean percentage free sulphur
4	2.3	0.62 0.62	0.62
5	2.4	0.64 0.64	0.64
6	2.5	0.65 0.65	0.65
24	2.6	0.65 0.65	0.65

The results of these analyses indicate that the new procedure yields figures which are closer to those given by the Castle Mills method than are the results with the American method. Furthermore, at the conclusion of the oxidation by the new procedure, there is /

is very little insoluble residue, and the destruction of the organic substances is practically complete.

Finally, two samples of 2 grams each were extracted for 6 hours and oxidised by the new procedure. The usual method for the volumetric determination of benzidine sulphate was then followed, unused perchloric acid being removed as the insoluble potassium salt, chloric acid being reduced by means of hydroxylamine hydrochloride and the sulphate finally precipitated from faintly acid solution by excess of a dilute solution of benzidine hydrochloride. The results obtained - 0.65% and 0.64% - average 0.65%, suggest that a rapid and accurate estimation of the sulphur content of an acetone extract may be possible with this procedure.

It is proposed to continue this investigation along the following lines.-

Parallel analyses will be performed on all the vulcanised samples already prepared by the bromine method of the Rubber Division of the American Chemical Society and by the new procedure involving oxidation with nitric and perchloric acids and bromine followed by volumetric determination of the sulphuric acid as benzidine sulphate. The samples will be extracted /

extracted with acetone for varying periods. Additional vulcanised samples will be prepared containing accelerators of vulcanisation and will be subjected to similar series of analyses. In this way it is hoped to arrive at a conclusive comparison between the American method and the new procedure, and also at the minimum times of extraction for various types of vulcanised rubber compatible with accuracy of free sulphur estimation.

It has been suggested by Sir James Walker that more rapid extraction of the uncombined sulphur might be effected by the use of methyl-ethyl ketone in place of acetone (dimethyl ketone), or by working at pressures higher than atmospheric, since either procedure would lead to solution of the sulphur at a higher temperature. It is hoped to act on these suggestions in the near future.

Summary /

Summary.

A review has been made of the more important aspects of the literature concerning the determination of total sulphur in rubber. Considerable attention has been given to the work of Dekker, partly on account of the inaccessibility of one of his papers [12] to most rubber chemists, but in the main because his papers have been the most comprehensive of recent publications on the subject.

Vulcanised standard samples have been prepared and calibrated by analysis for total sulphyr by the Carius method. These have been used to test the accuracy of a new rapid procedure for total sulphur with satisfactory results. The new method involves oxidation by means of nitric and perchloric acids and bromine, followed by volumetric estimation as benzidine sulphate of the sulphuric acid produced.

The more recent of previous publications concerning the estimation of free sulphur in rubber have been discussed. A suggested new procedure for free sulphur has been detailed, the results of some preliminary analyses have been given, and the lines along which further study will be conducted have been indicated.

The /

The author desires to take this opportunity of expressing his gratitude to his employers, The North British Rubber Co. Ltd., for facilities given to pursue this investigation and for permission to publish the results in their present form.

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